

## SLURRY FISCHER - TROPSCH SYNTHESIS IN CHINA

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### INTRODUCTION

China is one of a few countries where coal is used as major energy source. Research and development of clean coal technology is especially important for China to solve the problems of environmental pollution and to increase supply of liquid fuel especially the unleaded high quality gasoline. It is well known that slurry Fischer - Tropsch synthesis technology (SFTST), which has the advantages on both technology and economics over traditional fixed process as demonstrated by Sasol's Slurry Phase Distillate Process, is an advanced technology of indirect liquefaction of coal. Institute of coal chemistry has developed SFTST on both catalysts and a micro-pilot unit (MPU) as well as chemical engineering since 1986. The present paper will summarize the status and progress in R & D of SFTST.

### 1 CATALYST

One of the key problems in the development of SFTST is to provide a catalyst with high activity, good selectivity and long catalyst life. Iron catalysts, which are not only hydrogenation catalysts, but also active water gas shift catalysts, are indeed the most promising one as commercial catalyst for SFTST.

The catalysts used in our laboratory were prepared in a continuous multistage stirred precipitation reactor similar to those described by Kölbel<sup>[1]</sup>. Preparation conditions of catalyst including precipitation temperature, pH value and promoters were examined. Typical catalyst composition was 99.5 Fe; 0.5 Cu; 0.29 K<sub>2</sub>O by weight. The pretreatment condition and synthesis results were shown in table 1. From both hydrocarbon yield and time on stream in table 1, it is evident that the synthesis results based on temperature-programmed method are better than those based on non-programmed method. P2 pretreatment was preferred in the long life test by considering the same ratio of H<sub>2</sub>/CO in both pretreatment and synthesis. In order to understand the phase change during catalyst pretreatment, XRD analyses of fresh catalyst and catalyst partially induced at the initial stage and the later stage of pretreatment were compared and shown in Fig. 1. Crystal phase of a fresh catalyst is totally hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) as shown in Fig. 1 A. XRD of the catalyst partially induced at the initial stage of pretreatment as shown in Fig. 1 B indicated that magnetic iron oxide and Hägg carbide began to appear, but Hematite still existed. Fig. 1 C is XRD spectrum of the catalyst induced at the later stage of pretreatment. Hematite disappeared totally and magnetic iron oxide and Hägg carbide were the dominant crystal phase. Above results are significant to judge the extent of pretreatment of catalysts. Three long life tests were conducted in a magnetically stirred 1L autoclave. The results are given in table 2. It is found that iron catalysts prepared had longer life time and thus they were applied in MPU for SFTST.

### 2 MICRO - PILOT UNIT

Schematic of MPU is shown in Fig. 2. After being purified and preheated to a given temperature, syngas with relatively low H<sub>2</sub>/CO ratio (0.5 - 1.5) was bubbled through a slurry of unsupported precipitated iron catalysts suspended in wax medium in BCSR. The gas distributor was a porous sintered metal plate. The catalyst used was the unsupported precipitated iron catalyst promoted by copper and potassium with a particle size less than 44 $\mu$ m. Suspended catalyst was separated from reactor - wax by sedimentation in the settling vessel. The catalyst was recirculated between the enlarged upper section and the bottom of the BCSR through a settling vessel and an 2L autoclave in sequence. Catalyst settling tests on the MPU demonstrated that catalyst concentrations were 0.92wt% at 130°C and 0.66wt% 200°C in the wax withdrawn from the section of the settling vessel for the same settling time. It is clear that increasing settling temperature makes it easier to separate catalyst from the reactor - wax. On the other

hand, catalyst concentration in the reactor - wax approaches a constant value as settling time is extended. Therefore, a reasonable settling time can be set up to raise the efficiency of the settling vessel. Operation of separation was conducted every twelve hours. The reactor - wax, in which catalyst concentration was maintained at 0.5 - 0.8wt%, was regularly withdrawn through an overflow outlet. The enlargement of BCSR plays reducing the concentration of catalyst in the slurry entering the settling vessel, and the autoclave is used for the addition and activation of make - up catalyst. Fig. 3 shows variation of catalyst concentration in the reactor - wax with time on stream during the duration test lasted for over 1000h. The ranges of process variables were as follows: 260 - 280°C (1st - stage)/320 - 340°C (2nd - stage), 1.4 - 2.4 MPa, 2.0NL/gFe · h(1st - stage)/500 - 1000h<sup>-1</sup>(2nd - stage) and ratio of H<sub>2</sub>/CO 0.5 - 1.5. Mean results of the test were as follows: syngas conversion (once - through) 65.1%, yield of C<sub>3</sub><sup>+</sup> 100g/nm<sup>3</sup>(CO + H<sub>2</sub>), total hydrocarbon production > 350g/gFe. When CO - rich syngas was used, the yield of C<sub>3</sub><sup>+</sup> was 110g/nm<sup>3</sup>(CO + H<sub>2</sub>). Examples of material balances on a 12 hrs basis are given in table 3. Heat of reaction for FT synthesis from heat balance at 280°C for 1st - stage BCSR is 2938.5kJ/m<sup>3</sup>(CO + H<sub>2</sub>), which is fairly consistent with 2829.6kJ/m<sup>3</sup>(CO + H<sub>2</sub>) reported by farley<sup>[2]</sup> and 3038.9kJ/m<sup>3</sup>(CO + H<sub>2</sub>) calculated by stoichiometry equation. During the duration test, catalyst samples were taken from 1st - stage BCSR at various time on stream for Mossbauer spectroscopic study of iron catalyst and the phase present in the samples were unchanged due to isolation of the sample surrounded with the reactor - wax from ambient. Fig. 5 shows the corresponding phase composition of iron catalyst in BCSR run as a function of time. It is found that the fresh catalyst was 64% of α - Fe<sub>2</sub>O<sub>3</sub> and 36% of SP + Fe<sup>3+</sup>. The trend with time in the bulk phase composition of catalyst shows that while the extent of reduction and carburization extent of iron catalysts increased with extending time on stream and approached to the steady state with reducing fraction of magnetite. This is in accordance with the results reported by Satterfield et. al. <sup>[3]</sup> for fused magnetite catalysts. It is therefore considered that slurry phase operation is favorable of reduction and carburization of iron catalyst to keep catalyst activity and stability constant.

The duration test demonstrated that the performance of operation in the MPU was satisfactory. Its temperature control, flow system and other equipment were reliable. Viscosity of slurry was basically constant throughout the test. The design of the slurry recirculation loop was reasonable with less loss of catalyst and stable operation.

### 3 Support studies

#### 3.1 Solubilities and Mass transfer coefficients

Equilibrium gas solubilities (C<sub>eq</sub>) and volumetric liquid - side mass transfer coefficients (k<sub>La</sub>) were measured for hydrogen and monoxide in n - paraffin, n - octacosane and FT300 wax at various pressure (1.0 - 4.0MPa) temperatures (100 - 300°C), and a rotate speed of 800rpm in a 1l. agitated autoclave. In the range of operating conditions investigated the relationships of gas equilibrium solubilities with temperature and heats of solution were obtained as shown in table 4. The k<sub>La</sub> values for hydrogen and carbon monoxide in all liquid used increased with temperature and pressure, but decrease with increasing liquid molecular weight as shown in Fig. 5.

#### 3.2 Kinetic parameter and mathematic simulation

Based on the data obtained from BCSR in MPU, the kinetic parameters of the Fischer - Tropsch synthesis (FTS) on unsupported precipitated Fe - Cu - K catalysts were estimated with a multi - component BCSR model. The main assumptions of the BCSR model under steady state conditions are as follows: 1. Plug flow gas phase and unmixed slurry phase; 2. the main mass transfer resistance to diffusion being at the liquid side of the gas - liquid interface; 3. uniform catalyst concentration throughout the BCSR; 4. FTS reaction rate expression being:

$$-R_{H_2+CO} = kC_{H_2} / (1 + KC_{CO_2}/C_{CO}) \quad (H_2/CO \leq 0.8) \quad \text{where } k = k_0 \exp(-E_a/RT - \beta t)$$

The parameter values estimated were  $k_0 = 1.36 \times 10^8 \text{ cm}^3/\text{gcat. s}$ ,  $E_a = 100.0 \text{ kJ/mol}$ ,  $K = 0.204$ . Table 5 gives comparison of kinetic parameters obtained with those reported by Kuo<sup>[4]</sup> and Sanders<sup>[5]</sup>. It is seen from table 5 that kinetic parameters estimated are very close to values reported. The results predicted from FTS rate expression indicated that activity of catalyst used will deactivated by 1% after 35 h on stream, 26% after 1000h and 50% after 2300 h. It is obvious that the stability of the catalyst used should be improved. Also, axial concentration profiles of H<sub>2</sub>, CO, CO<sub>2</sub> in both gas phase and liquid phase and the effect of bubble size on syngas conversion were computed by the BCSR model and the kinetic parameters estimated. Axial concentration profiles of each

component in both gas and liquid phases are depicted in Fig. 6.

### 3. 3 Hydrodynamics

It is known that the FT reaction is a volume reducing reaction. The volume flow rate of gas phase is gradually diminished with increasing conversion. Therefore, phase holdup and axial solids concentration were investigated in a tapered bubble column (0.1m and 0.2m id on the top and bottom, respectively, 3m height) with slurry circulation in a system composed of air, water and quartz sand. The axial distribution of solid concentration was measured by the synchronously sampling method and gas holdup by pressure drop method. The effect of solid particle size (142.5 $\mu$ m, 180 $\mu$ m), solid concentration (0-100kg solid/m<sup>3</sup> slurry), slurry velocity (0-0.0157m/s) and gas velocity (0-0.125m/s) on gas holdup and solid axial concentration distribution were determined.

Experimental results were well agreement with the prediction made on the basis of the one dimensional sedimentation - dispersion model. The correlations of particle Peclet Number and gas holdup were obtained as follows;

$$Pe_p = 5.06 (Fr_g^2 / Re_g)^{0.130} (1 + 0.019 Re_p)$$

where  $0.03 \leq Pe_p \leq 0.4$ ;  $1166 \leq Re_g \leq 18843$ ;  $5.25 \leq Re_p \leq 10.45$ ;  $0.0064 \leq Fr_g \leq 0.104$

$$\frac{\epsilon_g}{(1 - \epsilon_g)^4} = 0.302 (g D^2 \rho_L / \sigma_L)^{0.125} \left( \frac{g D^3 \rho_L^2}{\mu_L^2} \right)^{0.083} (Fr_g)^{0.958}$$

### CONCLUSIONS

Unsupported precipitated Fe-Cu-K catalyst, which was prepared in a continuous precipitator, was applied in MPU. Catalyst activation proceeded well with syngas by the temperature-programmed method. The 1000h run demonstrated the SFTST at a micro-pilot scale. Operation and performance of the MPU were good. A preliminary measure of separation of catalysts from reactor-wax was realized by a slurry recirculation loop. Under conditions of 260-280°C (1st-stage)/320°C (2nd-stage), 1.5-2.5MPa, 2.0NL/gFe·h (1st-stage), 500-1000h<sup>-1</sup> (2nd-stage), and H<sub>2</sub>/CO ratio 0.6-0.7, a yield of C<sub>7</sub><sup>+</sup> over 100g/nm<sup>3</sup>(CO+H<sub>2</sub>) can be achieved. Engineering data and information including kinetic knowledge and solubilities are useful for further development of the process and scale-up and design of the BCSR.

### REFERENCES

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Table 1 Pretreatment conditions and results of synthesis reaction

Pretreatment						Synthesis reaction							
No.	H <sub>2</sub> /CO	T/°C	P	WHSV	Note	T/°C	P	WHSV	H <sub>2</sub> /CO	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	R.T.
1	1:0	260	1.5	2	B	260~280	1.5	2.0	2.4	a little liquid	-	-	-
2	A	280	0.3	2	C	260~280	1.5	2.0	2.0	92.9	45.9	432	
3	2:1	280	1.6	2	C	280	1.5	2.0	2.0	66.7	22.0	126	
4	2:1		0.4/0.9	2	P1	260~280	1.5	2.7	2.0	99.5	59.0	640	
5	1.5:1		0.3/1.0	2	P1	260~280	1.5/2.5	1.8/3.4	0.85	157.3	105	280	
6	1:1		0.3/1.0	2	P2	260~280	1.5/2.5	2.0	1.0	113.1	77.0	1112	

Note: R.T.—running time, h; A—N<sub>2</sub>/CO=9; B—isothermal 12 h; C—isothermal 24 h; P1—increasing and decreasing temperature at isorate, then pressuring again, total time 35 h; P2—temperature programmed pretreatment

Table 2 Results of the long life test

Run No.	A-26	A-30	B-6
Temperature / °C	250~280	250~280	260~280
Pressure / MPa	1.5~3.0	1.5~2.5	1.5~2.5
WHSV / L·g(Fc) <sup>-1</sup> ·h <sup>-1</sup>	2.96	2.88	2.96
H <sub>2</sub> /CO in feed	1	1	1
Hours on stream / h	1112	1128	1008
X <sub>CO</sub>	69.5	82.9	78.6
X <sub>H<sub>2</sub></sub>	40.4	52.7	36.3
X <sub>H<sub>2</sub>+CO</sub>	54.5	67.4	64.4
Hydrocarbon composition / %			
CH <sub>4</sub>	6.0	8.1	9.6
C <sub>2</sub> H <sub>4</sub>	4.8	5.0	4.1
C <sub>2</sub> H <sub>6</sub>	3.7	2.7	6.2
C <sub>3</sub> H <sub>6</sub>	7.3	6.2	4.7
C <sub>3</sub> H <sub>8</sub>	1.9	1.2	3.2
C <sub>4</sub> H <sub>8</sub>	6.8	4.5	7.4
C <sub>4</sub> H <sub>10</sub>	1.7	1.4	3.9
C <sub>5</sub> <sup>+</sup> minus wax trap	45.0	53.5	41.1
wax trap	18.6	14.4	13.1
Hydrocarbons yield			
C <sub>1</sub> <sup>+</sup> g/m <sup>3</sup> (CO+H <sub>2</sub> )	113.8	116.9	145.1
C <sub>5</sub> <sup>+</sup> g/m <sup>3</sup> (CO+H <sub>2</sub> )	77.0	83.5	91.2

Table 3 Material balance

Temperature/°C	265	265	265	270	275	280
Pressure/MPa	2.0	2.5	2.5	2.0	2.0	2.0
WHSV NL/gFe · h	2.15	2.24	2.26	2.23	2.28	2.31
H <sub>2</sub> /CO	0.61	0.62	1.32	0.60	0.60	0.66
X <sub>n<sub>2</sub>∞</sub> %	69.2	70.4	58.0	75.8	77.7	81.4
Inlet feed syngas NL · h <sup>-1</sup>	644	671	678	669	684	693
Outlet tail gas NL · h <sup>-1</sup>	377	385	416	354	355	336
Oil/g · h <sup>-1</sup>	16.5	17.3	22.8	23.1	23.8	24.8
Wax/g · h <sup>-1</sup>	50	49.7	30.6	50.2	53.1	54.8
Aqueous/g · h <sup>-1</sup>	10.4	12.0	26.4	11.3	12.4	16.0
Material recovery %	99.7	98.9	98.5	96.7	94.7	95.1
C†/g[Nm <sup>-1</sup> (CO+H <sub>2</sub> )] <sup>-1</sup>	133.6	143.2	132.2	149.2	154.4	163.0
C‡/g[Nm <sup>-1</sup> (CO+H <sub>2</sub> )] <sup>-1</sup>	113.1	115.2	90.0	123.7	127.1	129.9

Table 4 The correlations of gas equilibrium solubilities  
with temperature and Heats of solution

medium	H <sub>2</sub>		CO	
	Correlation	Heats of solution	Correlation	Heats of solution
paraffin	0.9892exp(-4697.9/T)	4697.9	0.9889exp(-2135.9/T)	2135.9
n-C <sub>22</sub> H <sub>46</sub>	0.9892exp(-5129.4/T)	5129.4	0.9889exp(-2609.9/T)	2609.9
FT300wax	0.9897exp(-8142.3/T)	8142.3	1.0108exp(-5276.6/T)	5276.6

Solubility, kmol/kg/atm, Heat of solution, J/mol

Table 5 Comparison of kinetic parameters

Investigator	catalyst	k <sub>a</sub> , cm <sup>3</sup> /gcat · s	E <sub>a</sub> , kJ/mol	K
Kuo (1983)	Fe—Cu—K	6.7 × 10 <sup>9</sup>	105.0	0.089
Sanders (1987)	Fe—K	1.42 × 10 <sup>9</sup>	88.2	0.316
Authors	Fe—Cu—K	1.36 × 10 <sup>9</sup>	100.0	0.204

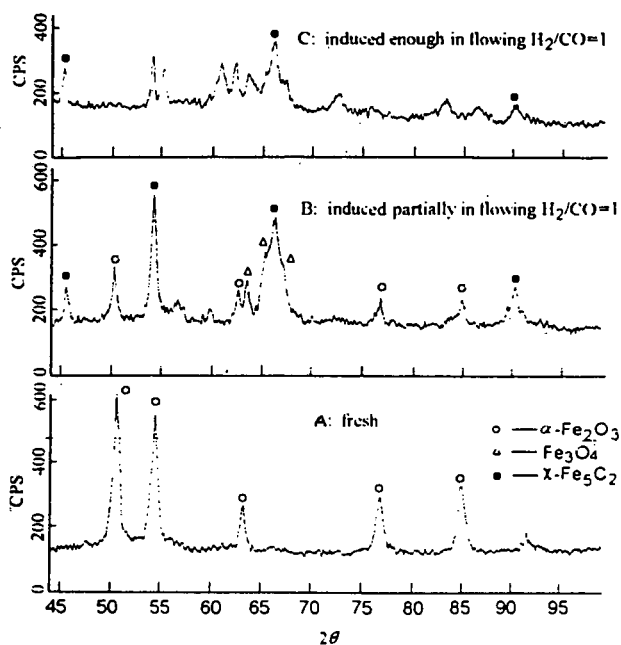


Fig. 1 XRD of the precipitated Fe - Cu - K catalyst

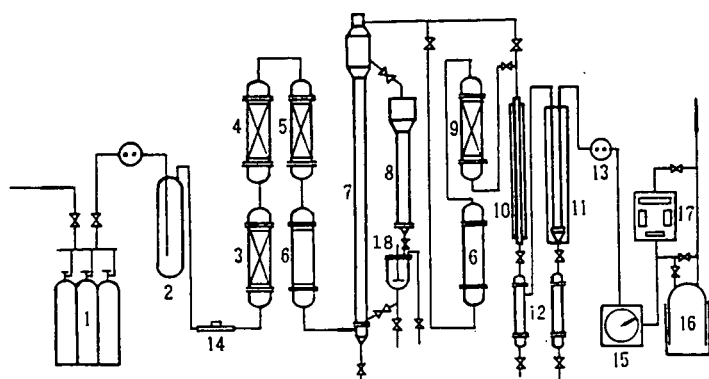


Fig. 2 A simplified flow diagram of the two - stage MPU for the synthesis of hydrocarbons

1. Syngas cylinder 2. Pressure buffer tank 3. Water trap 4. Iron carbonyl removal 5. Sulfide removal 6. preheater 7. 1st - stage BCSR 8. Settling vessel 9. 2nd - stage fixed - bed ZSM - 5 reactor 10. Air condenser 11. Chilled condenser 12. Liquid products receiver 13. Pressure let down valve 14. Mass flow meter 15. Wet - test meter 16. gas holder 16. IR gas analyzer 18. autoclave

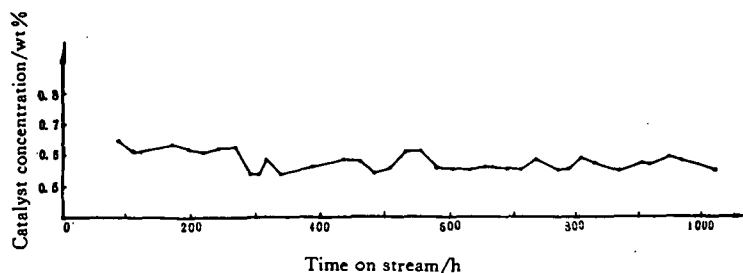


Fig. 3 Variation of catalyst concentration in the reactor - wax with time on stream

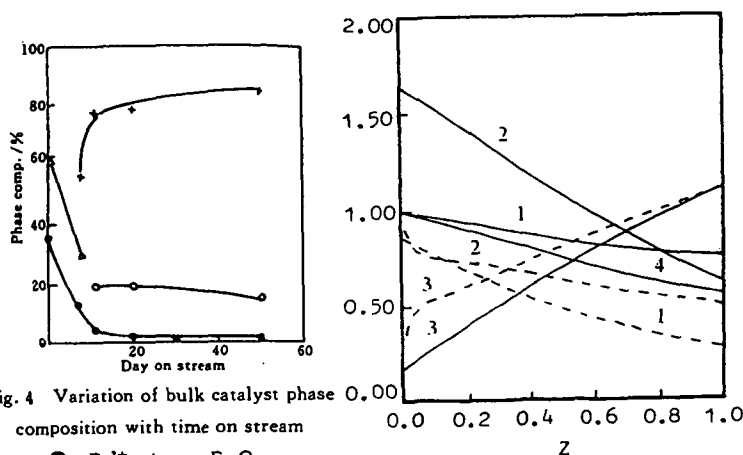


Fig. 4 Variation of bulk catalyst phase composition with time on stream

● —  $\text{Fe}^{2+}$ ;  $\Delta$  —  $\alpha\text{-Fe}_2\text{O}_3$ ;  
○ —  $\text{Fe}_3\text{O}_4$ ;  $\times$  —  $\gamma\text{-Fe}_2\text{C}_2$

liquid ---- gas —; 1.  $\text{H}_2$ , 2. CO, 3.  $\text{CO}_2$ , 4. U

Fig. 6 Dimensionless concentration profiles for each component and gas velocity profile

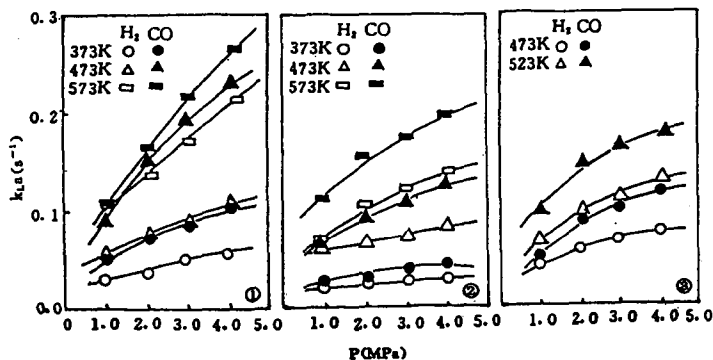


Fig. 5 Volumetric mass transfer coefficient  $k_{L,a}$  of  $\text{H}_2$ , CO in various liquids  
(① n - paraffin; ② n - octacosane; ③ FT300 wax)